

Electrets ed. by G. M. Sessler 3rd edition (Laplace Press,
Morgan Hill, California 1998) Vol. 1

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1. Introduction

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With 2 Figures

An electret is a piece of dielectric material exhibiting a *quasi-permanent electrical charge*. The term "quasi-permanent" means that the time constants characteristic for the decay of the charge are much longer than the time periods over which studies are performed with the electret.

The electret charge may consist of "real" charges, such as surface-charge layers or space charges; it may be a "true" polarization; or it may be a combination of these. This is shown schematically in Fig. 1.1 for a dielectric plate. While the true polarization is usually a frozen-in alignment of dipoles, the real charges comprise layers of trapped positive and negative carriers, often positioned at or near the two surfaces of the dielectric, respectively. The electret charges may also consist of carriers displaced within molecular or domain structures throughout the solid, resembling a true dipole polarization. If the charges are displaced to domain boundaries they are referred to as Maxwell-Wagner polarization. On metallized electrets, a compensation charge may reside on the electrode, unable to cross the energy barrier between metal and dielectric. Mostly, the net charge on an electret is zero or close to zero and its fields are due to charge separation and not caused by a net charge.

An electret not covered by metal electrodes produces an *external electrostatic field* if its polarization and real charges do not compensate each other everywhere in the dielectric. Such an electret is thus in a sense the electrostatic analogue of a permanent magnet, although electret properties may be caused by dipolar and monopolar charges while magnetic properties are only due to magnetic dipoles. The existence of an external field and the corresponding analogy with a magnet has often been used to define the electret.

However, as *Heaviside* already realized in 1892 [1.1], the fields of an electret may be compensated within a short time period by the relative motion of real charges and dipoles. This is observed in many piezoelectric substances. If one prefers to include some of these materials in the electret category, as *Heaviside* did, it is necessary to use the broader definition of the electret introduced above based on the *permanency of at least one of its charge components* and waive the necessity of an external field. However, such a broad definition includes the entire class of piezoelectric substances. We shall in the following adhere to this definition but include from the group of piezoelectric materials only the polymeric substances in the discussions in this book (see also Sect. 1.3).

While the classical electrets were made of *thick plates of carnauba wax* or similar substances, present electret research frequently deals with *thin-film*

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Upon cooling and renewed heating under a field of opposite polarity, a current I_2 occurs. For dipole polarization, one obtains during the second heating a superposition of a charging and a discharge current of equal magnitude, so that $|I_2| = |2I_1|$. Such a relation does not hold for charge separation and charge injection, and one has generally $|I_2| < |2I_1|$ in these cases [2.115].

In certain materials, such as alkali halides, space-charge effects can be generated by irradiation with light of band-gap energy. Thermal depolarization of such a sample will uncover the TSC spectrum due to these charges and thus allow one to distinguish it from the dipolar depolarization spectrum [2.116].

Identification of polarization effects is also possible by comparing thermally stimulated current (TSC) measurements of electrets with dielectric data. The relationship between dielectric constant and dielectric loss factor on one hand and the charges and currents released due to dipole reorientation during TSC on the other hand have been derived by *van Turnhout* [2.29] (see also Sect. 3.9). Similar relations also exist between dilatometric and TSC measurements. For example, the correspondence of TSC and dielectric or dilatometric data allows one to identify the polarization phenomena responsible for the α and β peaks in polar polymers, where they are related to dipole orientation.

Information about the nature of electret polarizations can also be gained from piezoelectric and pyroelectric measurements, as discussed in Chap. 5. Finally, other experiments such as electron-spin resonance [2.117], birefringence and singleharmonic generation [2.85], and infrared and X-ray studies [2.118] can, in principle, shed light on the electret effect. For example, far-infrared spectroscopy and X-ray studies have shown that poling of PVDF induces structural rearrangements in the crystalline parts of the polymer [2.118]. We refer, however, to the literature for a detailed discussion of these methods. Some additional information about methods for distinguishing between polarization and real charges is given in Sect. 3.4.

2.6 Permanent Dipole Polarization and Real-Charge Storage

Permanent dipole polarization and charge storage have been discussed under a variety of aspects and a host of experimental data is documented in the literature. Much of this information is, however, of purely academic interest today. To keep the material to be reviewed within reasonable limits, only some recent and representative results are presented. Much of the older information on thermoelectrets and photoelectrets is anyhow well covered in the literature [2.25].

The permanent dipole polarization and charge retention achievable in various electret-forming materials depends to a large degree on material properties and environmental conditions. Of the large number of insulators investigated with respect to electret properties, those of particular importance are certain inorganic crystals, some polymer materials and a number of (more

historically interesting) waxes. To be useful for electret studies these substances have to show either suitable polar properties or extremely low conductivity due to a large number of deep trapping centers (see Sect. 1.2). Generally, both of these features are not found in the same material. It appears that most dielectrics with polar properties have an undesirably high conductivity. This can be partly attributed to the hygroscopic behavior of many polar substances which causes conductivity increases due to absorption of water. On the other hand, the lowest-conductivity materials are relatively nonpolar (see Table 1.1).

2.6.1 Retention and Decay of Dipole Polarization

The dipolar polarization of inorganic crystals may be caused by *structural properties* of the crystal lattice, as found in many of the piezoelectric substances, or it may be due to *lattice imperfection or doping*, for example in impurity-vacancy dipole systems of alkali halides. In polymers and waxes, dipole properties can similarly originate from *polar groups* in the crystalline parts of the polymer or from *imperfections or impurities*. An example for the former is the monomer group in PVDF and for the latter the carbonyl groups in polyethylene. A considerable amount of information about the nature of dipolar effects has been obtained from TSC measurements, in the case of dipole relaxation often referred to as "ionic thermocurrent" measurements (see Chap. 3).

The saturation polarization P_p , expected after a sufficiently long polarizing time depends, according to (2.47), on the polarizing field E as

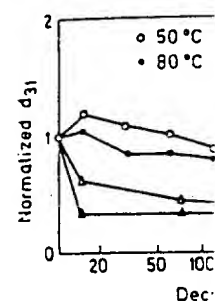
$$P_p = \epsilon_0(\epsilon_s - \epsilon_\infty)E. \quad (2.73)$$

Experimental data of $P_p/\epsilon_0 E$ for a few polymers as determined from current integrals of TSC curves are shown in Table 2.1. The results are evaluated separately for two different dipolar phenomena, referred to as the β and α relaxations, which manifest themselves as two distinct TSC peaks. While the β relaxation is due to motions of the side groups of the molecular chains, the α relaxation is caused by joint motion of side groups and main chains (see also Sect. 3.2). A comparison with the corresponding values of the dipolar strength $\Delta\epsilon = \epsilon_s - \epsilon_\infty$ indicates good agreement between $P_p/\epsilon_0 E$ and $\Delta\epsilon$ for the β peaks; however, for the α peaks $P_p/\epsilon_0 E$ is higher than $\Delta\epsilon$, which may be partially due to superposition of space-charge motions.

The proportionality between P_p and E breaks down if the dipole alignment is approaching saturation. This occurs generally for fields of about $1 \text{ MV} \cdot \text{cm}^{-1}$ and values of P_p around $1 \mu\text{C} \cdot \text{cm}^{-2}$, if poling temperature and time are sufficient. For example, PVDF assumes a maximum polarization of $12 \mu\text{C} \cdot \text{cm}^{-2}$ [2.8, 119, 120]. This represents a significant alignment of the molecules available in the dielectric since the calculated maximum polarization for β -phase PVDF is about $22 \mu\text{C} \cdot \text{cm}^{-2}$ (see Sect. 5.7).

Table 2.1. Released charges from PVDF foils [2.29, 119]

Polymer
Polymethyl methacrylate
Polyethylene terephthalate
Polyvinyl chloride (PVC)
Polyfluorethylene propylene
Poly(vinylidene fluoride)



A detailed account of the polarization of PVDF of space charges can be found in the literature. We refer to the literature for details.

Results on the decay of polarization together with simulation are shown in Figure 2.1.

The decay of polarization process, controlled by the decay time constant, is valid for the case of isothermal decay and for isothermal decay.

$$P_p(t) = P_p(0) \exp(-t/\tau)$$

More general forms of the decay process are possible under non-isothermal conditions and for non-isothermal decay.

Observed decay of polarization indicating a distribution of relaxation times or a distribution of energies or a distribution of such relaxation times isothermal decay is evidenced by the decay of polarization.